

Highlights from recent literature

1 Analytical

1.1 Determination of gold in precious metal alloys by microwave digestion and potentiometric titration with ferrous sulfate

A novel potentiometric titration method for detection of Au using FeSO_4 as a titrant was proposed. L Zhu, Y Zhao, K Li, L Yang, G Yang, Y Guan, Y Jin, Z An, Y Liu, Yunjie from the Kunming Institute of Precious Metals, Kunming, 650106, Peop. Rep. China, *Yejin Fenxi* (2008), **28(5)**, 14. The microwave digestion and pretreatment for precious metal alloys were researched. The conditions of improving accuracy and precision for titrn. of Au were discussed. The proposed method was compared with former national std. of China and fire assaying method. The Au, Pt and Pd alloys could be decomposed rapidly in $\text{HCl-H}_2\text{O}_2$ by microwave heating digestion. A great deal of interferential elements of Pt, Pd, Rh, Ir, Sn and others were precipitated with CuCl . The analytical results were of accuracy and precision, with relative std. deviation 0.019-0.223% for detg. Au from 3-99.5%, and were in good accord with coulometry and fire assaying method. The developed method was satisfactorily applied to anal. of Au in Au, Pt and Pd alloys, Au powder, jeweleries, natural Au, solution, metallurgy materials, and so on.

1.2 Nano-roughness in gold revealed from X-ray signature

The authors present a new method for investigating roughness for surface structure and internal inhomogeneity down to the nano-scale for thin, nano-structured and opaque materials. J Glover, C Chantler, M de Jonge from the School of Physics, University of Melbourne, Australia, *Physics Letters A*, 2009, **373(12-13)**, 1177. The method uses careful measurements of the X-ray mass-attenuation coeff. and is applied to measure the magnitude of the roughness of gold foils. The technique is unique, providing insight into both surface and internal roughness. The authors show that moments of the distribution function of surface and internal structure can be investigated using this method, and discuss observable signatures.

2 Catalysis

2.1 The enhancement by water molecules of the catalytic activity of gas-phase and supported gold photocatalytic mineralization of benzene over gold containing titania nanotubes: role of adsorbed water and nanosize gold crystallites

Well aligned titania nanotubes, with surface area of .apprx.150 $\text{m}^2 \text{g}^{-1}$ and average pore diameter of .apprx.5 nm, have been synthesized by subjecting a mesoporous TiO_2 sample to alk. treatment followed by calcination at different temperatures S Awate, R Sahu, M Kadgaonkar, R Kumar, MGupta, Catalysis Division, National Chemical Laboratory, Pune, 411008, India, *Catalysis Today*, 2009, **141(1-2)**, 144. Composite catalysts with gold particles dispersed in these nanotubes were also synthesized and their structural, morphology, optical and photocatalytic properties were examined. The catalytic activity of TiO_2 for UV-mediated photo-oxidation of benzene was found to be affected by several factors, such as the sample texture, presence of adsorbed water and gold crystallites. The overall conversion of benzene to form CO_2 followed a trend: Au/nanotube > TiO_2 nanotubes > mesoporous TiO_2 . In situ IR spectroscopy revealed that the adsorption and reaction of benzene mols. gave rise to formation of certain phenolic species over TiO_2 , while the temperature-programmed desorption (TPD) study showed that the Au/ TiO_2 interfaces serve as distinct sites for the adsorption and activation of oxygen mols. It is suggested that certain hydroxyl and oxygen ion radicals produced under UV-irradiation may promote the deep oxidation of surface phenolic species and phenoxyl ($\text{ArO}\cdot$) type transient radicals.

2.2 Gold particle size determination on $\text{Au/TiO}_2\text{-CeO}_2$ catalysts by means of carbon monoxide, hydrogen chemisorption and transmission electron microscopy

Au/TiO_2 and $\text{Au/TiO}_2\text{-CeO}_2$ catalysts were prepared by the sol-gel method and carbon monoxide, hydrogen chemisorption and TEM spectroscopy have been exploited to detect the size of gold particles. The gold nanoparticles (8.1 to 2.1 nm) were deposited by using the deposition-precipitation method. C Guzman, G Del Angel, R Gomez, F Galindo, R Zanella, G Torres, C Angeles-Chavez, J Fierro from the Departamento de Quimica, Universidad Autonoma Metropolitana-Unidad Iztapalapa, 09340, Mex., *Journal of Nano Research*, 2009, **5**, 13-23. The XRD characterization shows the presence of anatase as the TiO_2 cryst. phase; while by XPS spectroscopy, the presence of Au, Au_2O_3 , Ce^{3+} and Ce^{4+} species co-existing in the $\text{Au/TiO}_2\text{-CeO}_2$ catalysts is shown. The characterizations by TPD-CO as well as by TPD- H_2 (temperature programmed desorption) showed that on catalysts containing cerium, the gold particle size can be detected with great accuracy by using these chemisorption methods. The gold particle size calculated from either the

CO or H₂ thermodesorption values is in good agreement with that obtained by High Resolution Transmission Electron Microscopy (HRTEM) and Scanning Transmission Electron Microscopy (STEM) analyses. It was proposed that the TPD-CO and/or TPD-H₂ techniques could be helpful for the characterization of the gold particles by TEM; esp. when the high contrast in the pictures of the supports containing CeO₂ prevents the particle size from being detected.

2.3 Thermal stability and catalytic activity of gold nanoparticles supported on silica

2.5 Nm gold nanoparticles were grown on a fumed silica support, using the phys. vapor deposition technique of magnetron sputtering, that are thermally stable when annealed in an oxygen containing environment up to at least 500.degree.. G Veith, A Lupini, S Rashkeev, S Pennycook, D Mullins, V Schwartz, C Bridges, N Dudley from the Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA, *Journal of Catalysis*, 2009, **262**(1), 92. Traditional Au/TiO₂ catalysts rapidly sinter to form large 13.9 nm gold clusters under these annealing conditions. This surprising stability of Au/SiO₂ is attributed to the absence of residual impurities (ensured by the halide-free prodn. method) and a strong bond between gold and defects at the silica surface (about 3 eV per bond) estd. from d. functional theory (DFT) calcns. The Au/SiO₂ catalysts are less active for CO oxidation than the prototypical Au/TiO₂ catalysts, however they can be regenerated far more easily, allowing the activity of a catalyst to be fully recovered after deactivation.

2.4 New insight on the nature of catalytically active gold sites: Quantitative CO chemisorption data and analysis of FTIR spectra of adsorbed CO and of isotopic mixtures

FTIR absorption spectra of CO, of 12CO-13CO isotopic mixtures and of CO-18O₂ interaction on gold catalysts supported on group IV oxides are reported together with CO quant. chemisorption data. A Chiorino, M Manzoli, F Menegazzo, M Signoretto, F Vindigni, F Pinna, F Bocuzzi from the Department of Inorganic, Physical and Materials Chemistry and NIS Centre of Excellence, Universita di Torino, Turin, 10125, Italy, *Journal of Catalysis*, 2009, **262**(1), 169. On Au/TiO₂ two kinds of metallic gold surface sites, mutually interacting, adsorb CO in spite of the low CO/Au ratio (0.03). On Au/ZrO₂, where a CO/Au ratio of 0.30 has been detected, mutually interacting corner sites on non-metallic gold nanoclusters are present. Finally, isolated and neg. charged gold nanoclusters have been evidenced on Au/CeO₂. Different absorption coeffs. have been found. On all samples, by contacting CO-18O₂ at 90 K, only C16O18O is produced: gold sites are involved in the activation of both mols. The largest amount of C16O18O is produced on the CeO₂ supported sample, as a consequence of an easier activation of the oxygen on the anionic gold clusters and on the support.

2.5 Beneficial interaction of gold and palladium in bimetallic catalysts for the selective oxidation of benzyl alcohol

Bi- and monometallic nanoparticles of Au and Pd with a rather narrow size distribution were deposited on polyaniline (PANI) and their structural properties as well as catalytic behavior in the aerobic oxidation of benzyl alc. were investigated. S Marx, A Baiker from the Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, CH-8093, Switz., *Journal of Physical Chemistry C*, 2009, **113**(15), 6191. The size of the mono- and bimetallic particles was controlled in a narrow range (2.4-3.7 nm) using a colloidal preparation route. Admixing Pd to Au resulted in a strong enhancement of selectivity to benzaldehyde reaching a max. of 98% at full conversion at 100°C with bimetallic particles containing Au/Pd in a ratio of 1:9. Pure Au particles were significantly more active than pure palladium particles of the same size. Chem., structural, and electronic properties of the bimetallic catalysts were characterized using high angle annular dark field scanning transmission electron microscopy, at. absorption spectroscopy, XPS, and X-ray absorption spectroscopy. The PANI-supported nanoparticles showed a core shell structure with an Au enriched core and a Pd rich shell. The electronic changes occurring upon admixing Pd to Au were examined with X-ray absorption near-edge spectroscopy and XPS. The binding energy of core level electrons and the valence d-band occupation in the bimetallic particles were significantly altered in comparison to the monometallic particles, which together with the core shell structure is supposed to be the main reason for the observed changes in the catalytic behavior.

2.6 Interface structures of gold nanoparticles on TiO₂ (110)

Scanning transmission electron microscopy and d. functional theory are used to characterize at. structures of nanoscale heterointerfaces between Au nanoparticles and a TiO₂ (110) surface. N Shibata A Goto, K Matsunaga, T Mizoguchi, S Findlay, T Yamamoto, Y Ikuhara from the Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo, 113-8656, Japan, *Physical Review Letters*, 2009, **102**(13), 136105/1. When the Au nanoparticle size is smaller than a few nanometers, Au atoms preferentially attach to specific sites on the TiO₂ surface and thus form an epitaxial and coherent heterointerface. Conversely, as the Au size becomes larger, the Au-TiO₂ interface loses lattice coherency to accommodate the large lattice mismatch between the 2 dissimilar crystals.

2.7 Interaction of gold with cerium oxide supports: CeO₂(111) thin films vs. CeOx nanoparticles

Morphology, electronic structure, and CO adsorption of gold supported on well-ordered CeO₂(111) thin films and CeOx nanoparticles were studied by scanning tunneling microscopy (STM), photoelectron spectroscopy (XPS), and IR reflection

absorption spectroscopy (IRAS). M Baron, O Bondarchuk, D Stacchiola, S Shaikhutdinov, H Freund, Department of Chemical Physics, Fritz Haber Institute, Max Planck Society, Berlin, 14195, Germany, *Journal of Physical Chemistry C*, 2009, **113**(15), 6042. Ceria nanoparticles grown on cryst. thin silica films possess Ce in both the 3+ and 4+ oxidation states, with the former dominating in smaller particles. Upon deposition on CeO₂(111) films, most of the Au particles are formed at the step edges. The particles on terraces grow presumably through the decoration of point defects, which are more numerous on reduced surfaces. Combined XPS and IRAS data show that partially charged Au^{δ+} species are formed by deposition at low temperatures (apprx. 100 K) and low coverages on both ceria supports. Formation of Au^{δ+} on CeO₂(111) films is kinetically limited and is attributed to the interaction of the gold ad-atoms with defects. In variance to extended ceria surfaces, where only metallic Au nanoparticles are observed at 300 K, the cationic gold species are formed in abundance on nano-CeO_x and exhibit enhanced thermal stability. Nanoceria stabilizes small Au clusters, which may even be incorporated into the ceria nanoparticles at elevated temperatures.

2.8 Nanoporous Au: an unsupported pure gold catalyst?

The unique properties of gold especially in low temperature CO oxidation have been ascribed to a combination of various effects. In particular, particle sizes below a few nanometers and specific particle-support interactions have been shown to play important roles. In contrast, recent reports revealed that monolithic nanoporous gold (npAu) prepared by leaching a less noble metal, such as Ag, out of the corresponding alloy can also exhibit a remarkably high catalytic activity for CO oxidation, even though no support is present. A Wittstock, B Neumann, A Schaefer, K Dumbuya, C Kuebel, M; Biener, V Zielasek, H Steinrueck, M Gottfried, J Biener, A Hamza, M Baeumer, Institute for Applied and Physical Chemistry, University of Bremen, Bremen, 28359, Germany, *Journal of Physical Chemistry C*, 2009, **113**(14), 5593. Therefore, it was claimed to be a pure and unsupported gold catalyst. The authors investigated npAu with respect to its morphology, surface compn., and catalytic properties. In particular, we studied the reaction kinetics for low temperature CO oxidation in detail, taking the mass transport limitation due to the porous structure of the material into account. Results reveal that Ag, even if removed almost completely from the bulk, segregates to the surface, resulting in surface concentrations of up to 10 atom %. Data suggest that this Ag plays a significant role in activating of mol. oxygen. Therefore, npAu should be considered a bimetallic catalyst rather than a pure Au catalyst.

2.9 Kinetics of CO oxidation catalyzed by supported gold: a tabular summary of the literature

A review providing a tabular summary of the literature concerning the kinetics of CO oxidation catalyzed by supported Au is given. V Aguilar-Guerrero, B Gates from the Department of Chemical Engineering and Materials Science, University of California, Davis, CA, 95616, USA *Catalysis Letters*, 2009, **130**(1-2), 108. Tabular data state: how the catalysts were made, treated, and tested; catalyst phys. properties (e.g., average Au particle size); and kinetic data (turnover frequency, reaction order, apparent activation energy).

2.10 Gold catalysts supported on ceria doped by rare earth metals for water gas shift reaction: influence of the preparation method

Gold catalysts based on ceria, doped by various RE metals (La, Sm, Gd, Yb, Y) were studied. element. The influence of the preparation methods on structure, properties and catalytic activity in the WGS reaction was investigated. The catalysts' supports were prepared using two different methods: co-precipitation (CP) and mechanochem. activation (MA). D Andreeva, I Ivanov, L Ilieva, M Abrashev, R Zanella, J Sobczak, W Lisowski, M Kantcheva, G Avdeev, K Petrov, Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, 1113, Bulg., *Applied Catalysis, A: General* 2009, **357**(2), 159. The catalysts were tested in a wide temperature interval without and after reactivation. All samples were characterized using a combination of X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), Raman spectroscopy (RS) and XPS and TPR.

It was found that the catalytic activity of MA catalysts is higher than CP ones. The gold catalysts based on ceria doped by Yb and Sm exhibited the highest activity. After reactivation in air the MA samples almost kept the WGS activity same, while the CP catalysts increased it. The catalysts of a single- and double-phase structure are formed as a result of CP and MA prep., resp. There are no big differences in the gold particles size (2-3 nm) depending on dopants and on the preparation techniques. The RS spectra anal. indicates that most probably the oxygen vacancies are adjacent to Me³⁺ dopant and the ceria structure seems to be better ordered than in the case of alumina as a dopant. There is no distinct correlation between reducibility and WGS activity. The XPS anal. disclose pos. charged gold particles in addition to metallic gold within a surface region of fresh samples and only metallic gold on the samples after catalytic processing. There is no simple correlation between the concn. of Ce³⁺ in the samples and their WGS activity.

2.11 Selective deactivation of gold catalyst

The progressive poisoning effect of different mols. on carbon supported gold catalysts has been evaluated during the aerobic oxidation of glucose. C Della Pina, E Falletta, M Rossi,

A Sacco, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, CNR-ISTM, Università Degli Studi di Milano, Milan, 20133, Italy, *Journal of Catalysis* 2009, **263**(1), 92. A geometrical model has been derived for describing the morphology properties of two catalysts made of carbon supported gold particles having a known size distribution centered at 3.30 and 7.89 nm resp. The observed deactivation trend follows the order thiocyanate > cyanide .apprxq. cysteine > thiourea and it obeys an exponential law. The kinetics of catalyst deactivation has been interpreted by considering the important contribute of electronic factors which overlap the space shielding of active sites, due to long range poison-catalyst interaction influencing the entire metal particle. Considering the nature of the mols. showing a high poisoning effect and the promoting effect of OH-, a mol. model for electronic interactions in gold nanoparticles during the aerobic oxidation of glucose has been proposed where the dioxygen reduction step is differently influenced by soft and hard-nucleophiles.

2.12 Catalysis by gold: why size matters

A review; bulk gold is the most inert metal of all, however, when gold is finely dispersed on a support, it can be a very active catalyst for oxidation and hydrogenation reactions. X-ray absorption spectroscopy showed that the smaller the gold particles are, the shorter the gold-gold bond length is. J van Bokhoven, Institute for Chemical and Bioengineering, ETH Zurich, Zurich, CH-8093, Switz., *Chimia*, 2009, **63**(5), 257. The smaller particles also have an altered electronic structure, as they undergo less hybridization between the s, p, and d orbitals than the larger particles. The d band narrows and moves closer to the Fermi level. As a result, hydrogen, oxygen, and CO adsorb on the metal surface and the nano-sized metal particles can become catalytic.

2.13 Thermodynamics and kinetics of the adsorption of carbon monoxide on supported gold catalysts probed by static adsorption microcalorimetry: the role of the support

The interaction of carbon monoxide and oxygen with gold particles supported on zinc oxide, alumina, and titania was investigated by microcalorimetry. Multiple processes were detected during CO adsorption, including adsorption of CO on the gold particles and support, oxidation of CO, and formation of carbonates. X Xia, J Strunk, W Busser, M Comotti, F Schuth, M Muhler, Laboratory of Industrial Chemistry, Ruhr-University Bochum, Bochum, D-44780, Germany, *Journal of Physical Chemistry C* (2009), **113**(21), 9328. The rate of O₂ adsorption was much slower than that of CO adsorption. The heats and entropies of CO adsorption on the Au sites indicated that the interaction between CO and Au supported on TiO₂ is much stronger than that between CO and Au supported on ZnO. The Au/ZnO sample had the largest amount of lattice oxygen (7.6 .mu.mol/g), which reacted with CO to give CO₂.

2.14 Gold nanoparticles supported on manganese oxides for low-temperature CO oxidation

A series of Au catalysts deposited on various single-phase Mn oxides (MnOx including MnO₂, Mn₂O₃, Mn₃O₄) were examined for their performance in low-temperature CO oxidation Au was deposited on the MnOx support by deposition-precipitation with urea (DP urea). Au/MnOx catalyst activity for CO oxidation strongly depended on the nature of the MnOx support, ranked in the order: Au/Mn₂O₃ > Au/MnO₂ > Au/Mn₃O₄. L Wang, Q Liu, X Huang, Y Liu, Y Cao, K Fan, Department of Chemistry & Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai, 200433, Peop. Rep. China, *Applied Catalysis, B: Environmental* 2009, **88**(1-2), 204. Transmission electron microscopy results showed different Au particle size distributions for these catalysts; the Au/Mn₂O₃ catalyst exhibited the highest Au dispersion. Temperature-programmed reduction experiments indicated that Au/MnOx catalyst reproducibility followed the same sequence as catalyst activity. XPS results suggested metallic and cationic Au species existed in the Au/Mn₂O₃ catalyst; only metallic Au species were present in the other catalysts. The unique surface redox properties of Mn₂O₃ demonstrated great superiority for Au nano-particle anchoring and dispersion, which led to a higher reducibility of Mn₂O₃ and Au/Mn₂O₃ activity for CO oxidation.

2.15 Morphological controlled synthesis and catalytic activities of gold nanocrystals

The authors report a convenient and efficient procedure for controlling the morphologies of gold nanocrystals via varying the mol. structure of polyols. Y Bi, G Lu, State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, Peop. Rep. China, *Materials Letters*, 2008, **62**(17-18), 2696. The gold nanostructures, from nanoplate to mixtures of rod, plate, and sphere, and nanosphere, can be synthesized quant. with 1,3-propylene glycol, 1,2-propylene glycol, and glycerol, resp. The authors speculate that polyols with diverse position and no. of OH group play an important role in detg. the geometric structures and morphologies of the final products. It may be due to the specific interaction between OH groups and Au³⁺ ions, which affect selective growth of various planes of gold nanocrystals. The catalytic activity of the obtained different shaped gold nanocrystals for hydrogen prodn. from formaldehyde solution at room temperature also was studied. The gold nanoplates exhibit higher catalytic activities than spherical gold nanoparticles and the mixtures of rod, plate, and sphere.

2.16 Creation of catalytic functions by minimizing the size of gold

A review on the development of Au catalysts, mechanisms of catalytic activities, and application to air purifn., H manuf., and green chem. M Haruta, Masatake, Grad. Sch. Urban

Environ. Sci., Tokyo Metropolitan University, Hachioji, 192-0397, Japan, *Seramikkusu*, 2009, **44**(5), 377.

2.17 Desorption of CO on supported gold nanoparticle catalysts: a comparative study

The adsorption of CO on three different gold nanoparticle catalysts supported on high surface area TiO_2 was studied using IR transmission spectroscopy at room temperature and CO pressures typically used in CO oxidation reactions. H Hartshorn; C Pursell, B Chandler, Department of Chemistry, Trinity University, San Antonio, TX, 78212-7200, USA, *Journal of Physical Chemistry C*, 2009, **113**(24), 10718. The three, real-world catalysts were Au catalysts synthesized in our lab. from thiol monolayer protected clusters (MPCs) and two com. catalysts from the World Gold Council (WGC and AuTEK). Within exptl. reproducibility, the adsorption data for the three catalysts are indistinguishable. While showing approx. Langmuir behavior, the adsorption data also show coverage dependence, as others have observed for many catalyst systems. Two approaches were used to fit the data, a two-site model and a variable binding const. model. The two-site Langmuir model yielded strong (36%) and weak (64%) binding const. of 2740 and 146 atm⁻¹, resp. Alternatively, using a sliding-tangent Langmuir fit gave a variable binding const. of 2670-120 atm⁻¹ at room temperature for coverage $\theta = 0-0.8$. The heat of adsorption was then extd. from the binding const. using a literature value for $-\Delta H$. These values were detected as $\Delta H = -64$ and -56 kJ/mol for strong and weak binding according to the two-site model and $\Delta H = -63$ to -56 kJ/mol for coverage $\theta = 0-0.8$ for the variable binding const. model. These values agree well with literature values obtained (i) using supported catalysts under higher pressures and (ii) using model catalysts under higher pressures and ultrahigh vacuum conditions.

2.18 Particle size effects of gold on the kinetics of the oxygen reduction at chemically prepared Au/C catalysts

Au nanoparticles with narrow and controlled size distributions were synthesized chem. and deposited onto a C support. Using the resulting Au on C (Au/C) catalysts, Au particle size effects on the kinetics of the oxygen reduction reaction (ORR) were analyzed in acidic media (0.5M H_2SO_4). T Inasaki; S Kobayashi, HFRE Division, Department of Chemistry, School of Science, Japan Science Technology Agency (JST), The University of Tokyo, ERATO, Bunkyo-ku, Tokyo, Hongo, 113-0033, Japan, *Electrochimica Acta* (2009), **54**(21), 4893. From rotating ring-disk electrode (RRDE) voltammetric studies, for bulk Au, the no. of electrons, n , involved in the ORR was nearly const. at potentials >-0.2 V. On the contrary, for the catalysts with diameters $<10-15$ nm, the value of n increased as the potential became more neg., and the highest value of n was obtained when the size of Au

particles was <3 nm. Further reduction of H_2O_2 or direct 4-electron reduction of O_2 proceeded at relatively low overpotential on extremely small Au clusters.

2.19 Effect of pretreatment atmosphere on CO oxidation over $\alpha\text{-Mn}_2\text{O}_3$ supported gold catalysts

Micro-structural properties of $\alpha\text{-Mn}_2\text{O}_3$ -supported Au catalysts moderately pretreated under different atmospheres (O_2 , He, H_2) in relation to their activity and stability for CO oxidation were assessed. L Wang, L He, Y Liu, Y Cao, Y He, K Fan, J Zhuang, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai, 200433, Peop. Rep. China, *Journal of Catalysis*, 2009, **264**(2), 145. Highest initial activity was obtained for the He-pretreated catalyst, which also suffered the most severe deactivation with time-onstream. O_2 pretreatment resulted in the best stability and highest steady-state activity among the 3 catalysts. Transition electron microscopy results showed that pretreatment had a negligible effect on Au particle size. While formation of moderate surface O vacancies prior to reaction was suggested to be responsible for the highest initial activity of He-Au/ $\alpha\text{-Mn}_2\text{O}_3$, over-reduction of the oxide support could explain inferior activity of the H_2 -pretreated catalyst. Based on x-ray photoelectron spectra and in-situ diffuse reflectance IR Fourier transform spectroscopy studies, the superior performance of the O_2 -pretreated $\text{O}_2\text{-Au}/\alpha\text{-Mn}_2\text{O}_3$ catalyst was attributed to creation of a specific O-enriched interface leading to an enhanced metal-support synergy.

2.20 NO reduction by CO over gold catalysts based on ceria supports, prepared by mechanochemical activation, modified by Me^{3+} ($\text{Me}=\text{Al}$ or lanthanides): effect of water in the feed gas

The reduction of NO by CO was studied over gold catalysts supported on ceria modified by Me^{3+} ions ($\text{Me} = \text{Al}, \text{La}, \text{Sm}, \text{Gd}$ and Yb). The ceria supports were prepared by mechanochem. activation. L Ilieva, G Pantaleo, R Nedyalkova, J Sobczak, W Lisowski, M Kantcheva, A Venezia, D Andreeva, Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, 1113, Bulg. *Applied Catalysis, B: Environmental* 2009, **90**(1-2), 286. The samples were characterized using XRD, TPR, XPS and Raman spectroscopy. According to the XPS data the concn. of the oxidized gold species was higher than that of metallic gold in the fresh samples modified by lanthanides. On the fresh samples modified by Al only a small part of metallic gold existed in oxidized state. After the catalytic test, only metallic gold was found on the lanthanide-containing catalysts, while on the Al-modified catalyst a small amount of oxidized Au species in addition to metallic Au was detected. No substantial differences in the average particle sizes of gold, the lattice parameters and the average size of ceria particles were observed. The nature of the modifier and

the applied method of ceria supports preparation and gold deposition detected most likely the differences observed in the Raman and TPR data, as well as the catalytic activity results. The catalytic tests were performed under two different conditions: (i) in the presence of H₂ in the gas feed and (ii) adding also water to the gas feed. The lowest activity was observed over the Al-containing catalyst under dry feed, which correlates with the TPR results. The addition of water to the feed led to a significant improvement of the NO and CO conversions over all of the samples studied. At 200°C, Yb-containing gold catalyst exhibited the highest NO and CO conversions. Very promising results for the selectivity toward N₂ were achieved using the lanthanides as dopants. In contrast to the gold supported on Al-doped ceria, no NH₃ formation was observed within the whole temperature interval up to 400°C over gold catalysts supported on ceria modified by La, Sm, Gd or Yb.

3 Chemistry

3.1 Selective detection of hexachromium ions by localized surface plasmon resonance measurements using gold nanoparticles/chitosan composite interfaces

Selective removal of hexavalent Cr ions from aq. solutions using a chitosan/Au nanoparticles composite film was demonstrated. K Fahnestock, M Manesse, H McIlwee, C Schauer, R Boukherroub, S Szunerits, Department of Materials Science and Engineering, Drexel University, Philadelphia, PA, 19104, USA, *Analyst* (Cambridge, United Kingdom) 2009, **134**(5), 881. Localized surface plasmon resonance (LSPR) was used to measure the interface stability and detect the incorporation of Cr ions over time. The effects of pH, EDTA, and various foreign ions such as trivalent Cr, Na, Ca, phosphate, sulfate and chloride on the adsorption of hexavalent Cr were studied.

3.2 Size-dependent stability of supported gold nanostructures onto ceria: an HRTEM study

Gold nanoparticles of various sizes, supported onto ceria, were synthesized using both deposition-precipitation and coprecipitation methods. J Majimel, M Lamirand-Majimel, I Moog, C Feral-Martin, M Treguer-Delapierre, ICMCB/CNRS, Université de Bordeaux, Pessac, 33608, Fr. *Journal of Physical Chemistry C*, 2009, **113**(21), 9275. Whatever the size, the study of the Au/CeO₂ interface confirms the existence of two preferential orientation relationships with a dislocation network which compensates the 25% interfacial lattice mismatch. Behaviors of supported gold nanostructures under the electron beam were examined by high-resolution transmission electron microscopy (HRTEM). The thermal stability of the gold nanostructures was found to be strongly affected by the particle size. For small nanostructures (<5 nm), reversible shrinkage of gold layer by layer onto ceria

surface was observed. For larger ones, a progressive and irreversible encapsulation by a CeO₂-x layer was found and a four-step process was experimentally underlined.

3.3 Effect of sulfate pretreatment on gold-modified TiO₂ for photocatalytic applications

The influence of sulfated pretreatment of TiO₂ on the structure, morphology, and dispersion of gold and photocatalytic properties of Au/TiO₂ were studied. M Hidalgo, M Maicu, J Navio, G Colon, Instituto de Ciencia de Materiales de Sevilla, Consejo Superior de Investigaciones Científicas (CSIC), Universidad de Sevilla, Seville, 41092, Spain, *Journal of Physical Chemistry C*, 2009, **113**(29), 12840. Notable enhancements in the photocatalytic activity of TiO₂ were achieved by deposition of gold onto samples that had previously undergone sulfate treatment followed by high temperature calcination. The enhancement in activity can be attributed to the stronger bonding and improved electronic communication between gold particles and TiO₂ on defect rich surfaces as are found on sulfated samples after calcination at 700°C. Two different methods for gold deposition were evaluated: chem. reduction by citrate and photodeposition. The citrate method produced more homogeneous and smaller gold particles with a better dispersion than photodeposition, which lead to greater increases in activity in the photocatalytic degrading of phenol when the former method was used for deposition on both sulfated and nonsulfated TiO₂. The combination of sulfate pretreatment and gold deposition by chem. reduction was shown to be a good strategy to obtain gold/titania catalysts possessing homogeneous particle size and dispersion of the metal and a strong bonding between the Au and the TiO₂ surface.

4 Electrochemistry

4.1 Electrical control of plasmon resonance of gold nanoparticles using electrochemical oxidation

A large shift of the localized surface plasmon resonance (LSPR) spectrum of Au nanoparticles was attained by electrochemical oxidation of the nanoparticle surface. This oxidation occurred in the cell, which consisted of a pair of In Sn oxide (ITO) electrodes and H₂O medium between the electrodes. T Miyazaki, R Hasegawa, H Yamaguchi, H Oh-oka, H Nagato, I Amemiya, S Uchikoga, Electronic Imaging Laboratory Corporate Research and Development Center, Toshiba Corporation, 1, Komukai-Toshiba-cho, Saiwai-ku, Kawasaki, 212-8582, Japan, *Journal of Physical Chemistry C*, 2009, **113**(19), 8484. On one side of the ITO electrode, the Au nanoparticles were adsorbed. With the application of a voltage of 5 V to the cell, a spectrum shift as large as 68 nm was obtained. Though the spectrum shift has already been observed by changing liq. crystal (LC) orientation surrounding Au nanoparticles, the size of the shift was not large (11 nm). That was because the variation of the effective refractive

index of LC was rather small. The large shift due to electrochem. oxidation resulted from the large refractive index of Au-O. The electrochem. oxidation was confirmed by XPS anal. of the Au nanoparticles with the LSPR spectrum shift. Other possible mechanisms of the shift such as charge localization, aggregation, and adsorption of charged materials proved to have no effect via SEM measurement and so on. This large shift of the resonance spectrum can be expected to lead to further development of spatial light modulators for next-generation optical communications and displays.

4.2 Structure dependent electrooxidation of small organic molecules on Pt-decorated nanoporous gold membrane catalysts

The electrocatalytic properties of self-supported Pt-decorated nanoporous gold (Pt-NPG) membranes towards the electrooxidation of formic acid and some other small organic mols. is described. X Ge, R Wang, S Cui, F Tian, L Xu, Y Ding, Key Laboratory of Liquid Structure and Heredity of Materials, Ministry of Education, Shandong University, Jinan, 250061, Peop. Rep. China, *Electrochemistry Communications*, 2008, **10**(10), 1494. By effectively enhancing the Pt utilization and providing a unique surface structure, the electrooxidation of formic acid on Pt-NPG was found to be highly sensitive to its surface structure. An unparalleled increase by .apprxeq.2 orders of magnitude in catalytic activity was achieved on NPG electrodes decorated with sub-monolayer Pt atoms, as compared to the com. Pt/C catalyst under the same testing conditions.

4.3 Determination of kinetic and diffusional parameters for sodium borohydride oxidation on gold electrodes

Direct borohydride fuel cells are among the latest fuel cell types under research and development. There is a need for further elucidation of the borohydride electrochemical oxidation and potential step experiments were carried out with a Au disk electrode in alk. Na borohydride solutions of varying concentrations and temperatures Anal. of the current transients for the full time scale identified the domains where diffusion, electron transfer, and mixed control prevail. D Santos, C Sequeira, Institute of Materials and Surfaces Science and Engineering, Department of Chemical and Biological Engineering, Instituto Superior Tecnico, TULisbon, Lisbon, 1049-001, Port., *Journal of the Electrochemical Society*, 2009, **156**(5), F67 Chronoamperometric measurements in the diffusion-controlled region led to current responses exhibiting Cottrellian behavior, from which accurate diffusion coeffs., D, were estd. Arrhenius plots of D allowed detection of the diffusion activation energies and max. diffusion coeffs. Chronocoulometric measurements generated Anson plots from which the kinetic rate constns. and charge transfer activation energies were calculated Anal. of the current

densities in conditions of infinite mass transfer led to Tafel plots from which exchange current densities, transfer coeffs., std. rate constants and standard activation energies for charge transfer were detected Purely charge-transfer regimes were not recognized in the studied system under the imposed potentials.

5 Electronics and sensors

5.1 Manufacturable, highly responsive gold nanowire mercury sensors

The authors have developed a manufacturable and highly responsive gold nanowire sensor capable of detecting ppb concentrations of mercury in air and water. S Keebaugh, W Nam, S Fonash, Center for Nanotechnology Education and Utilization, The Pennsylvania State University, University Park, PA, USA, *NSTI Nanotech 2007, Nanotechnology Conference and Trade Show, Santa Clara, CA, United States, May 20-24, 2007* (2007), **Volume 3**, 33-36. Editor(s): Laudon, Matthew; Romanowicz, Bart. Publisher: CRC Press, Boca Raton, Fla. The nanowire sensor exhibits a superior response compared to thin film sensors and we have observed that this response is closely related to the morphology of the nanowire. By carefully controlling the sensor fabrication steps, the authors are able to obtain reproducible smooth, continuous nanowire morphologies and consequently obtain highly responsive and reproducible sensors. Additionally, these nanowire sensors are very robust and capable of withstanding regeneration temperatures without significant changes in the nanowire morphology or baseline elec. properties.

6 Medical and dental

6.1 Influence of anchoring ligands and particle size on the colloidal stability and in vivo biodistribution of polyethylene glycol-coated gold nanoparticles in tumor-xenografted mice

Polyethylene glycol (PEG)-coated (pegylated) gold nanoparticles (AuNPs) have been proposed as drug carriers and diagnostic contrast agents. G Zhang, Z Yang, W Lu, R Zhang, Q Huang, M; Tian, L Li, D Liang, C Li, Department of Experimental Diagnostic Imaging, The University of Texas M.D. Anderson Cancer Center, Houston, TX, 77030, USA, *Biomaterials*, 2009, **30**(10), 1928. However, the impact of particle characteristics on the biodistribution and pharmacokinetics of pegylated AuNPs is not clear. We investigated the effects of PEG mol. wt., type of anchoring ligand, and particle size on the assembly properties and colloidal stability of PEG-coated AuNPs.

The pharmacokinetics and biodistribution of the most stable PEG-coated AuNPs in nude mice bearing s.c. A431 squamous tumors were further studied using ¹¹¹In-labeled AuNPs. AuNPs coated with thioctic acid (TA)-anchored PEG

exhibited higher colloidal stability in phosphate-buffered saline in the presence of dithiothreitol than did AuNPs coated with monothiol-anchored PEG. AuNPs coated with high-mol.-wt. (5000 Da) PEG were more stable than AuNPs coated with low-mol.-wt. (2000 Da) PEG. Of the 20-nm, 40-nm, and 80-nm AuNPs coated with TA-terminated PEG5000, the 20-nm AuNPs exhibited the lowest uptake by reticuloendothelial cells and the slowest clearance from the body. Moreover, the 20-nm AuNPs coated with TA-terminated PEG5000 showed significantly higher tumor uptake and extravasation from the tumor blood vessels than did the 40- and 80-nm AuNPs. Thus, 20-nm AuNPs coated with TA-terminated PEG5000 are promising potential drug delivery vehicles and diagnostic imaging agents.

6.2 Intravascular photoacoustic imaging with gold nanoparticles

Intravascular photoacoustic (IVPA) imaging can image atherosclerotic plaques inside the artery by utilizing the differences in optical absorption between various tissue types. B Wang, E; Yantsen, T Larson, S Sethuraman, K Sokolov, S; Emelianov, Department of Biomedical Engineering, University of Texas at Austin, Austin, TX, 78712, USA, *Proceedings – IEEE Ultrasonics Symposium*, 2007, (Vol. 2), 848. Combined intravascular ultrasound (IVUS) and IVPA imaging has the potential to visualize both the structure and composition of plaques. However, the mol. or cellular specific components of the plaques can be further enhanced by introducing plasmonic nanoparticles as molecularly targeted contrast agents. To demonstrate that IVPA imaging with optical contrast agents is possible, we performed IVUS and IVPA imaging of a vessel phantom containing murine macrophages with gold nanoparticles inside the cells. Several controls including gold nanoparticles suspended in gelatin and macrophages without nanoparticles were also imaged. The results of our study suggest that IVPA is capable of imaging using gold nanoparticles as contrast agents. In addition, spectroscopic IVPA imaging can be used to distinguish aggregated nanoparticles from other tissue components and non-aggregated nanoparticles thus further enhancing the contrast of targeted components in the artery.

6.3 Cell up-take control of gold nanoparticles functionalized with a thermoresponsive polymer

Surface decoration of gold nanoparticles with thermoresponsive polymers endows a temperature tunable colloidal system switchable for enhanced intracellular up-take. Gold nanoparticles (AuNP, 18 ± 11 nm-diameter) produced by laser ablation synthesis in liq. solution were surface coated with thermoresponsive thiol terminated poly-N-isopropylacrylamide-co-acrylamide co-polymer possessing a lower crit. solution temperature (LCST) at 37°C. S Salmaso, P Caliceti, V Amendola, M Meneghetti, J Magnusson,

G Pasparakis, C Alexander, Cameron, Pharmaceutical Sciences Department, University of Padua, Padua, 35131, Italy, *Journal of Materials Chemistry*, 2009, **19**(11), 1608. Under selected conditions about 3800 polymer chains were conjugated per particle.

The polymer coated nanoparticles were found to display thermosensitive properties, as in solution they exhibited reversible aggregation/deaggregation above and below the LCST, resp. Cell culture studies showed that the polymer decorated AuNP were located into human breast adenocarcinoma MCF7 cells treated at 40°C (12000 AuNP/cell) with more than 80-fold greater up-take compared to cells treated at 34°C with the same particles (140 AuN/cell). This difference is attributable to a “switching” of the polymer coating to a globule state at 37°C and an increased hydrophobicity of the particles with a simultaneous loss of the stealth’ properties of the polymer coating. By contrast, cell up-take of uncoated AuNP (about 6000 AuNP/cell) did not depend on the incubation temperature. These data show that good control of the AuNP cell up-take can be obtained with the new polymer-gold nanoconjugates, and suggest that these systems might find use for targeting cells in vitro by a small temperature change or in vivo in body sites, such as inflamed or tumor tissues, where a temperature variation is already present.

6.4 Enhanced x-ray irradiation-induced cancer cell damage by gold nanoparticles treated by a new synthesis method of polyethylene glycol modification

The authors explored a very interesting gold nanoparticle system-pegylated gold in colloidal solution-and analyzed its uptake by mice colorectal adenocarcinoma CT26 tumor cells and the impact on the cell’s response to x-ray irradiation. C Liu, C Wang, C Chien, T Yang, S Chen, W Leng, C Lee, K Lee, Y Hwu, Y Lee, C Cheng, C Yang, Y Chen, J Je, G Margaritondo, Institute of Physics, Academia Sinica, Taipei, 115, Taiwan, *Nanotechnology*, 2008, **19**(29), 295104/1. The authors found that exposure to polyethylene glycol (PEG) modified (‘pegylated’) 4.7 nm gold nanoparticles synthesized by a novel synchrotron-based method enhances the response of CT26 cells to x-ray irradiation. TEM and confocal microscopy revealed that substantial amounts of such nanoparticles are taken up and absorbed by the cells and this conclusion is supported by quant. induced coupled plasma (ICP) results. Std. tests indicated that the internalized particles are highly biocompatible but strongly enhance the cell damage induced by x-ray irradiation. Synchrotron radiation Fourier transform IR (SR-FTIR) spectromicroscopy analyzed the chem. aspects of this phenomenon: the appearance of C=O stretching bond spectral features could be used as a marker for cell damage and confirmed the enhancement of the radiation-induced toxicity for cells.

6.5 Cyclodextrin-covered gold nanoparticles for targeted delivery of an anti-cancer drug

The authors report on the therapeutic ability of a novel cyclodextrin-covered gold nanoparticle (AuNP) carrier for noncovalent encapsulation of an anti-cancer drug. C Park, H Youn, H Kim, T Noh, Y; Kook, E; Oh, H Park, C Kim, Department of Polymer Science and Engineering, Inha University, Incheon, 402-751, S. Korea, *Journal of Materials Chemistry*, 2009, **19(16)**, 2310. The surface of the AuNPs was functionalized with cyclodextrin as a drug pocket, anti-epidermal growth factor receptor (anti-EGFR) antibody as a targeting moiety, and poly(ethyleneglycol) (PEG) as an anti-fouling shell. .beta.-Lapachone, an anti-cancer drug, was efficiently encapsulated into the hydrophobic cavity of cyclodextrin on the surface of the AuNP carriers (AuNP-1). The glutathione-mediated release of .beta.-lapachone from the surface of AuNP-1 was demonstrated by an expt. with MCF-7 (low glutathione concn.) and A549 cells (high glutathione concn.). We also show that the introduction of an anti-EGFR antibody onto the AuNP carriers (AuNP-2) increased the intracellular uptake of AuNP carriers as compared with AuNP-1, which does not contain a targeting ligand. In the in vitro cytotoxicity study, AuNP-2 with .beta.-lapachone exhibited a higher apoptosis effect than that caused by AuNP-1 with .beta.-lapachone. This work suggests that AuNPs covered with cyclodextrin and tumor-targeting ligands may find useful applications for the development of nanoparticles with therapeutic and diagnostic modalities.

6.6 Gold nanoparticles: shining light on cancer treatment

A review. A Herwadkar, J Kishor; A Prajakta, Department of Pharmaceutical Sciences, Institute of Chemical Technology, Mumbai University, Mumbai, 400 019, India, *Nano Science and Nano Technology*, 2008, **2(2-3)**, 48. Many chems. are continuously being screened as antitumor agents. Advances were made to envisage site-specific delivery of chemotherapeutic drugs which can effectively reduce problems assocd. with drug resistance and toxicity. Tremendous progress was made in the exploitation of the photothermal properties of gold nanoparticles in therapeutics. Nanoparticles of gold, which are in the size range 10-100nm, undergo a plasmon resonance with light. This is a process whereby the electrons of the gold resonate in response to incoming radiation causing them to both absorb and scatter light. This effect can be harnessed to either destroy tissue by local heating or release payload mols. of therapeutic importance. Gold nanoparticles can also be conjugated to biol. active moieties, providing possibilities for targeting to particular tissues. The authors describe the recent studies regarding synthesis and use of such metal nanoparticles for early cancer detection and treatment.

6.7 On the medicinal chemistry of gold complexes as anticancer drugs

A review. I Ott, Institute of Pharmaceutical Chemistry, Technische Universitaet Braunschweig, Braunschweig, 38106, Germany, *Coordination Chemistry Reviews* (2009), **253**(11+12), 1670. Metal complexes have shown interesting preclin. and clin. results as antitumor drugs and platinum compds. are well established in current cancer chemotherapy. However, the platinum based treatment of tumoral diseases is massively hampered by severe side effects and resistance development. Consequently, the development of novel metallodrugs with a pharmacol. profile different from that of the platinum drugs is in the focus of modern medicinal chem. and drug design. Among the non-platinum antitumor drugs, gold complexes have recently gained considerable attention due to their strong antiproliferative potency. In many cases the cell growth inhibiting effects could be related to anti-mitochondrial effects making gold species interesting drug candidates with a mode of action different from that of the platinum agents. The spectrum of gold complexes described as antiproliferative compds. comprises a broad variety of different species including many phosphine complexes as well as gold in different oxidation states. This presentation gives an overview of the relevant medicinal chem. of known gold complexes with in vitro and in vivo tumor growth inhibiting properties.

7 Metallurgy, materials and coatings

7.1 Study on gold content in white karat gold alloy jewelry by cupellation method

The Au content in white karat Au alloy samples is detected by the cupellation method, and the effects of Au content with the test portion wt. of the proof Au and samples, the variety of cupels, and the additive amount of Cu and Ag on the testing results are studied. S Li, Y Li, National Jewelry Quality Supervision and Inspection Center, Beijing, 100101, Peop. Rep. China, *Baoshi He Baoshixue Zazhi*, 2008, **10(3)**, 23. At the same time, the accuracy of the results detected by cupellation method is also validated using ICP. When the test portion wt. of the proof Au and samples is reduced to 160.00-200.00 mg, there has no influence on the result of Au content. Resp. using Mg oxide and bone ash cupels, the result deviation of Au content in the samples is within the allowable deviation of the national stds. The result of Au content in samples is much more closed to the theoretical value by adding proper Cu in the proof Au. The additive amount of Ag (2.5 to 2.7 times equal to the wt. of the proof Au) in the proof Au and samples has no influence on the result of Au content. In the AEA Round Robin 2006, National Jewelry Quality Supervision and Inspection Center (NJQSIC) in China acquired much well testing result by using the cupellation method.

7.2 Gold nanoparticle arrays fabricated on a silicon substrate covered with a covalently bonded alkyl monolayer by electroless plating combined with scanning probe anodization lithography

Hexagonal nanoholes, in which an array of Au nanoparticles was located, were successfully fabricated on the basis of scanning probe anodization lithog. H Sugimura, S Nanjo, H Sano, K Murase, Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto, 606-8501, Japan, *Journal of Physical Chemistry C*, 2009, **113**(27), 11643. The lithog. has been conducted to draw nanopatterns on a hexadecyl self-assembled monolayer covalently bonded to a Si substrate through Si-C bonds. Using a conductive at. force microscope (AFM) probe as a point contact electrode, current was locally injected into the monolayer-Si sample. The monolayer was decomposed on the location where current injected. Subsequently, at this point, the substrate Si was anodized resulting in the formation of an oxide nanodot. Next, the oxide nanodot was selectively etched with HF in order to make a nanohole while the surrounding monolayer remaining unetched. As a result, a nanohole was formed at the current injected point. Employing the remained monolayer as an etch mask, the nanohole was further etched with NH₄F in order to prepare a well-defined hydrogen-terminated surface in the nanohole. The nanohole became hexagonal due to the anisotropic nature of Si etching with NH₄F. The lateral size of the fabricated nanohexagonal holes were in the range of 180 .apprx. 320 nm. Finally, electroless plating was applied to the sample. Au nanoparticles were selectively nucleated on the surface of the nanohole's bottom and walls. The particles with a diameter less than 10 nm were well-sepd. each other with a nucleation d. of 150,000 .mu. m⁻². The NH₄F etching was successful in order to control the nucleation manner for the fabrication of the Au nanoparticle array.

8 Nanotechnology

8.1 Simple one-step synthesis of water and organic media soluble gold nanoparticles with various shapes and sizes

Gold nanoparticles with an average diameter in the range 1-100 nm have been synthesized from HAuCl₄.cntdot.3H₂O in didodecyldimethyl ammonium bromide (DDAB) aq. solutions at room temperature S Moon, S Young; K Tohru; T Takafumi; The Institute of Science and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka, 567-0047, Japan, *Journal of Crystal Growth*, 2009, **311**(3), 651. The particle size could be controlled by the concn. of DDAB and HAuCl₄. cntdot.3H₂O, and reaction temperature An increase in DDAB concentration caused a change in the particle shape from spherical to triangular, rectangular or various shapes. Until the crit. concentration of DDAB, where the size of gold

nanoparticles seemed to prevent particle growth from aggregation, a small particle size and narrow size distribution were obtained. And DDAB-coated nanoparticles can be dispersed well in both water and organic solvent with a high colloidal stability.

8.2 Shape separation of gold nanorods using centrifugation

The use of centrifugation for efficient sepn. of colloidal gold nanorods from a mixture of nanorods and nanospheres was demonstrated. V Sharma, K Park, M Srinivasarao, School of Polymer Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA, 30332, USA, *Proceedings of the National Academy of Sciences of the United States of America*, 2009, **106**(13), 4981. The hydrodynamic behavior of nanoparticles of various shapes is elucidated, and the shape-dependent drag causes particles to have shape-dependent sedimentation behavior. During centrifugation, the nanoparticles undergo Brownian motion under an external field and move with different sedimentation velocities dictated by their T. Svedberg coeffs. (1940). This behavior causes a separation of particles of different shape and size. The theor. anal. and experiments demonstrate the viability of using centrifugation to shape-sep. a mixture of colloidal particles.

8.3 Coalescence behavior of gold nanoparticles

Tetraoctylammonium bromide (TOAB)-stabilized gold nanoparticles were fabricated. Y Wang, W Liang, C Geng, The Cultivation Base for State Key Laboratory, Qingdao University, Qingdao, 266071, Peop. Rep. China *Nanoscale Research Letters*, 2009, **4**(7), 684. After an annealing of the as-prepared nanoparticles at 300°C for 30 min, the coalescence behavior of gold nanoparticles was investigated using high-resolution TEM in detail. Two types of coalescence, one being an ordered combination of two or more particles in appropriate orientations through twinning, and the other being an ordered combination of two small particles with facets through a common lattice plane, were observed.

8.4 Growth of segmented gold nanorods with nanogaps by the electrochemical wet etching technique for single-electron transistor applications

The growth of multisegment nanorods comprising gold (Au) and sacrificial silver (Ag) segments (Au-Ag-Au or Au-Ag-Au-Ag-Au) using the electrochem. wet etching method is reported. V Nguyen, S Kumar, G Kim, School of Information and Communication Engineering, Sungkyunkwan University, Suwon, 440-746, S. Korea, *Nanotechnology*, 2009, **20**(12), 125607/1. The nanorods were fabricated using an alumina template of thickness 100 .mu.m and pore size of 200 nm. A variety of nanorods from single to seven segments comprising alternate Au and Ag segments were fabricated with better control of growth rate. The multisegment

nanorods were selectively etched by removing the Ag segments to create gaps in the fabricated nanorods. A careful investigation led to the creation of a wide variety of nanogaps in the fabricated multisegment nanorods. The size of the nanogap was controlled by the passage of current through the electrochem. process, and size below 10 nm was achievable at exchanged charges of .apprx.1 mC. A further lowering in the size of nanogaps was achieved by dilg. the silver plating solution and a segmented nanorod with nanogap (Au-nanogap-Au) of 3.8 nm at exchanged charges of 0.2 mC was successfully created. In additionally, segmented nanorods with two or more nanogaps (Au-nanogap-Au-nanogap-Ag) placed sym. and asym. on either side of the central Au segments were also created. A prototype of a single-electron transistor device based on segmented nanorods with two nanogaps is proposed. The results obtained could form the basis for the realization of quantum tunneling devices where the barrier thickness is very critical and demands values less than 5 nm. The encouraging results show the promise of multisegment nanorods for fabricating devices working at the de Broglie wavelength such as single-electron transistors.

8.5 Luminescence properties of gold nanorods

In this work the authors report on the luminescence properties of gold nanorods synthesized by a seed growth method in the presence of cetyltrimethylammonium bromide (CTAB) solutions F Toderas, M Iosin, S Astilean, Nanobiophotonics Laboratory, Institute for Interdisciplinary Experimental Research, Faculty of Physics, Babes-Bolyai University, Cluj-Napoca, 400271, Rom., *Nuclear Instruments & Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, 2009, **267(2)**, 400. The authors have found that the emission intensity is dependent on the aspect ratio and the degree of dispersivity of the gold nanorods. The observed emission is explained in the term of the enhancement effect of the elec. fields via coupling to the surface plasmon resonance in the rods.

8.6 A microfluidic microreactor for the synthesis of gold nanorods

A microfluidic microreactor for the synthesis of gold nanorods is fabricated using femtosecond pulse laser microfabrication techniques. D Day, M Gu, Centre for Micro-Photonics, Faculty of Engineering and Industrial Sciences, Swinburne University of Technology, Victoria, 3122, Australia *Nanotechnology*, 2009, **20(10)**, 105601/1. Femtosecond pulse lasers are able to etch a wide range of materials that are required for a microreactor, from the photomasks to the microheaters. The heating of the fluid in the microreactor is achieved through the design and fabrication of a microscale heating element incorporated onto the bottom surface of the microreactor which is capable of reaching temperatures greater than 130°C. Computational fluid dynamic simulations of the heating profile of an optimized microreactor show increased

heating performance with respect to a serpentine microreactor. The synthesis of gold nanorods is demonstrated in the optimized microreactor, based on a flow rate of 0.5 .mu.g min⁻¹.

8.7 Photochemical strategies for the facile synthesis of gold-silver alloy and core-shell bimetallic nanoparticles

The reduction of HAuCl₄ and AgNO₃ in aq. surfactant solutions by 2-hydroxy-2-Pr radical generated by the photochem. cleavage of 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propane-1-one, commercialized as Irgacure-2959 (I-2959), produces Au-Ag bimetallic nanoparticles with different compn., and architecture, alloys, and core-shells. C Gonzalez, Y Liu, J Scaiano, Centre for Catalysis Research and Innovation and Department of Chemistry, University of Ottawa, Ottawa, K1N 6N5, Can. *Journal of Physical Chemistry C*, 2009, **113(27)**, 11861. The nanoparticle architecture depends on the surfactant employed. The use of hexadecyltrimethylammonium chloride (CTAC) produces Au(core)-Ag(shell) nanoparticles, as expected on the basis of the redox properties of the two metals, whereas when the surfactant is sodium dodecyl sulfate (SDS), it promotes the formation of Au-Ag alloy nanoparticles; the effect is attributed to silver's Coulombic advantage that compensates for the fact that gold is a "more noble" metal. Both structures are characterized by UV-vis spectroscopy, transmission electron microscopy (TEM) and high-resolution transmission spectroscopy (HR-TEM).

8.8 Size-controlled synthesis of gold nanoparticles by a sodium diphenylamine sulfonate reduction process

Au nanoparticles have been prepared by the reaction of HAuCl₄ and sodium diphenylamine sulfonate in the presence of SDS (sodium dodecyl sulfate)/SDBS (sodium dodecyl benzene sulfonate) at room temperature Effect of varies of reactive conditions on the morphology and size of gold nanoparticles, such as the amount of the HAuCl₄, reductant and SDS, was examined resp. L Lai, Q Liu, H Rong, Z Chen, J Sun, Q Zhou, T Shang, Jiangsu Provincial Key Laboratory of Fine Petrochemical Engineering, Department of Chemical Engineering, Jiangsu Polytechnic University, Changzhou, 213146, Peop. Rep. China, *Huaxue Yanjiu Yu Yingyong*, 2009, **21(1)**, 18. The Au nanoparticles with average size 10, 14, 30 and 36nm can be obtained via controlling the reactive conditions, resp. The nanoparticles were characterized by transmission electron microscopy (TEM), UV-Visible light absorption spectrum. The research showed that the mol. of SDS or SDBS/HAuCl₄ has effect on the size of Au nanoparticles.

8.9 Highly controlled core/shell structures: tunable conductive polymer shells on gold nanoparticles and nanochains

Controls in coating gold nanoparticles with conductive polymers are reported, where uniform core/shell nanoparticles with tailored core aggregation and shell thickness are unambiguously demonstrated. In the presence of sodium dodecylsulfate (SDS), the adsorption and in situ polymn. of aniline or pyrrole on the surface of gold nanoparticles gives uniform polymer shells. S Xing, L Tan, M Yang, M Pan, Y Lv, Q Tang, Y Yang, H; Chen, Hongyu, Division of Chemistry and Biological Chemistry, Nanyang Technological University, 637371, Singapore *Journal of Materials Chemistry*, 2009, **19(20)**, 3286. A typical single encapsulation of 10 nm gold nanoparticles gave .apprx.99.1% monomers out of 1074 particles surveyed. The shell growth was found to be kinetically controlled; polyaniline was successively grown on 22 nm gold nanoparticles by multiple growth cycles, giving shell thicknesses of 14, 31, 61 and 92 nm, resp. We show that the aggregation of gold nanoparticles can be controllably promoted in this system, by simply timing SDS addition, to give linearly aggregated cores of 2-20 particles. The in situ formation of conductive polymer shells has allowed the isolation and unambiguous characterization of these nanochains for the first time. The one-step, "mix-and-wait" synthesis solely utilizes inexpensive starting materials and is, therefore, well-suited for fabrication of large quantities of core/shell nanoparticles. The core/shell nanoparticles form stable colloidal suspensions and can be readily purified by centrifugation.

9 Refining

9.1 Method of gold and silver recovery from concentrates

The invention refers to methods of gold and silver recovery from sulfide concs. and industrial deposited concs. M Medkov, V Molchanov, M Belobeletskaya, A Vovna from the Institut Khimii Dal'nevostochnogo Otdeleniya RAN, Russia; OOO "Gidrometallurg", Patent No RU 2351666, C1 April 2009. Method involves leaching gold-bearing and argentiferous concs. with acid thiocarbamide liquors with the oxidizer added and extrn. recovering noble metals from leaches. Extn. is preceded with adding thiocyanate ions to leaches in amount to ensure complete transferring thiocyanate gold and silver complexes into the organic phase. Extractant is mixed tri-Bu phosphate (TBP) and diphenylthiocarbamide (DPTC) in kerosene, containing TBP 1.5-2.0 mol/l and DPTC 0.015-0.022 mol/l. Gold and silver are re-extd. from the organic phase with the reducing agents pptg. noble metals within reduction process. Thus, lower thiocarbamide loss at the stage of noble metal extrn. from the leach.

9.2 Method for extracting gold from waste printed circuit boards

The title method comprises the steps of: (1) crushing waste printed circuit boards, pulverizing, and sepg. metals from plastic, (2) mixing the metals and 15-25 wt.% nitric acid solution at a wt. ratio of 1:(1-45), stirring at 10-80°C for 1-6 h, filtering, extg. Cu from the filtrate through ion membrane electrolysis, washing the filter residue, and oven-drying, (3) adding the filter residue into mixed solution (composed of primary iodine solution and an auxiliary oxidant 0.1-10 wt.%) at a wt. ratio of 1:(1-25), adjusting pH to 3-9 with an inorganic acid and basic solution, and reacting in a thermostatic vibrator at 10-60°C for 2-5 h, and (4) filtering, placing the filtrate in the cathode region of an electrolytic tank, placing secondary iodine solution (as the electrolyte) in the anode region, electrolyzing at 20-30°C, a voltage of 1-20 V, a current intensity of 0.01-0.4 A and a c.d. of 5-200 A/m² for 0.25-5 h, filtering the solution in the cathode region, and collecting the filter residue to obtain gold paste. In step 3, the primary iodine solution contains iodine 0.2-2.0 wt.%, water-sol. iodide and water, wherein the wt. ratio of iodine to water-sol. iodide is 1:(1-13). In step 4, the secondary iodine solution contains iodine 0.1-2.0 wt.%, water-sol. iodide and water, wherein the wt. ratio of iodine to water-sol. iodide is 1:(1-13). The method has high yield, low cost, and little pollution. D Chen, Q Xu, L Chen, M; Huang, C Chen, P Jiang, L Zhang, X Wang, Y Zhang from the Donghua University, Peop. Rep. China, Patent No CN 101392325, A, March 2009.

9.3 Study on extraction of gold from smelting slags

Using cyanidation method to leach gold from smelting slags, single- factor and orthogonal-test were used to study influencing factors. X Zhao, L An, College of Materials and Chemistry and Chemical Engineering, Chengdu University of Technology, Chengdu, 610059, Peop. Rep. China, *Youse Jinshu, Yelian Bufen*, 2008, **(3)**, 41. The resulted show that the leaching rate of gold could reach 82.60% in the conditions of 0.7% sodium cyanide, the pH of leaching solution amount to 11, the ratio of liq. to solid equal to three and agitation leaching 36 h in the remnant sediment. The leaching rate could be to 88.83% after ammonia water leached the copper and zinc.

9.4 Method for arsenic removal and gold leaching by microbial oxidation

Three *Thiobacillus ferrooxidans* strains with strong arsenic resistance and capacity of sulfide ore decompn., namely M1s, 1# and Malan, were used for a microbial oxidation and leaching expt. on DBF ore from Shimian County, Sichuan Province. X Tian, Y Wang, D Du, L Peng, Institute of Geomechanics, Chinese Academy of Geological Sciences, Beijing, 100081, Peop. Rep. China, *Wutan Yu Huatan*, 2008, **32(3)**, 298. The arsenic content and pH change in the microbial oxidation process and the optimum leaching conditions of gold were studied intensively. The change of

the microbial oxidation process with time and the optimum leaching conditions of gold are given in the paper.

9.5 Study on fluidized roasting of high-arsenic copper-bearing gold concentrate

High-arsenic copper-bearing gold conc. is roasted by fluidized bed roaster of BGRIMMDN150. The results show that dearsenic rate of 85%, desulfurization rate of 87%, copper acid-leaching rate of 83.2% and gold extn. of 94.96% are obtained under the roasting condition of weak oxide atm. Y Li, C Yuan, Y Wang, L; Sun, X Xu, Beijing General Research Institute of Mining and Metallurgy, Beijing, 100044, Peop. Rep. China, *Kuangye* (Beijing, China) , 2008, **17**(3), 33.

9.6 Technological specialties of flotation of gold mineral forms associated with sulfide minerals

Main trends in gold recovery increase from sulfide gold-bearing ores are considered, among them: optimization of ore-preparation processes, including electropulse treatment; combination application of sulfhydryl collectors of different mol. structure and collecting ability (xanthates, dithionic phosphates, thionocarbamates, dithiocarbamates) for recovery of finely disseminated gold; application of combination flow sheets based on chem.-metallurgical processes. V Ignatkina, V Bocharov, Moscow State Institute of Steel and Alloys (Technological University), Moscow, Russia, *Obogashchenie Rud (Sankt-Peterburg, Russian Federation)*, 2007, (4), 8-11.

9.7 Technological study and application on integrative recovery of gold, silver and platinum-group elements from refractory alloy gold

The researches on gold, silver and platinum-group elements separation from gold electrolysis anode slime were carried out. J Zhao, W Peng, Lingbao Jinyuan Tonghui Refinery Co., Ltd., Lingbao, Henan Province, 472500, Peop. Rep. China, *Huangjin*, 2008, **29**(7), 44. First, gold was reduced and separated after activation in several times. And then, platinum-group elements were recovered. The experimental results revealed that the recovery rate of gold and silver was obviously influenced by the addition amount and times of activator, smelting temperature and time. With 4 times addition of activator, the sepn. recovery rate of gold was about 90% after 2 h activation at the temperature of 1,100°C. After 2 times activation smelting and acid solution, the residual refractory alloy gold was turned into precious metal powder. And then gold was solved in aqua regia, and was reduced by sodium nitrite. The total recovery rate of gold was more than 99.9%. The recovery rate of high grade platinum-group elements concn. was more than 99%.

9.8 Ore processing tests in the west open-pit of Wulaga gold mine

The dissemination size of metal sulfides and gold-bearing minerals in the west open-pit of Wulaga gold mine is relatively fine. H Wang, F Yang, J Zhao, B Yang, S; Ren, Q Wang, Changchun Gold Research Institute, Changchun, Jilin Province, 130012, Peop. Rep. China, *Huangjin*, 2008, **29**(7), 37. With raw ore floatation, gravity concentration of gold conc., biol. oxidation of gravity concn. tailings, cyanidation leaching and zinc precipitation process, the total recovery rate of gold was 80.09%, and it was increased by 26.45% than the present technol. process. With raw ore floatation, gold conc. roasting, cyanidation leaching of roasting residue and zinc precipitation process, the total recovery rate of gold was 76.49%, and it was increased by 22.85% than the present technol. process. It was revealed that gold concentrate must be pretreated with oxidation process in order to enhance the gold recovery rate.